(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 April 2001 (19.04.2001)

PCT

(10) International Publication Number
WO 01/27194 A1

(51) International Patent Classification[7]: C08K 3/28, 5/16, 5/3492, C08L 27/12

(21) International Application Number: PCT/US00/03205

(22) International Filing Date: 8 February 2000 (08.02.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/415,596 8 October 1999 (08.10.1999) US

(71) Applicant: DYNEON LLC [US/US]; 6744 33rd Street North, Oakdale, MN 55128 (US).

(72) Inventors: GROOTAERT, Werner, M., A.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). MILLET, George, H.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). KOLB, Robert, E.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agent: LILLY, James, V.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States *(national)*: AE, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/27194 A1

(54) Title: FLUOROELASTOMER COMPOSITIONS AND ARTICLES MADE THEREFROM

(57) Abstract: A curable fluoroelastomer composition comprising (1) a fluoroelastomer comprising interpolymerized units derived from (a) at least one perfluoroolefin; (b) at least one perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof; and (c) a cure site component comprising at least one nitrile group, and (2) a catalyst composition comprising at least one ammonia-generating compound. Methods of curing such fluoroelastomer compositions and articles made from such fluoroelastomers are also provided.

FLUOROELASTOMER COMPOSITIONS AND ARTICLES MADE THEREFROM

Field of the Invention

This invention relates to fluoroelastomer compositions having nitrile group-containing cure site monomers. In another aspect, the invention relates to articles, including molded articles such as o-rings, seals and gaskets, made from curable fluoroelastomer compositions.

Background of the Invention

Fluoroelastomers (*i.e.*, elastomeric fluoropolymers) are polymeric materials that exhibit significant tolerance to high temperatures and harsh chemical environments. Consequently, fluoroelastomers are particularly well adapted for use as seals and gaskets and other molded elastomeric parts in systems that are exposed to elevated temperatures and/or corrosive chemicals. Such parts are widely used in the chemical processing, semiconductor, aerospace and petroleum industries, among many others.

The unique properties of fluoropolymers are attributable largely to the stability and inertness of the copolymerized fluorinated monomer units that make up the major portion of a polymer backbone. Perfluorinated monomers, such as tetrafluoroethylene, hexafluoropropene, and perfluorovinyl ethers are among such fluorinated monomer units. In order to develop the elastomeric properties of the fluorinated polymers completely, the polymers typically are cross-linked, *i.e.*, they are vulcanized. To accomplish this, a small percentage of a cure site monomer is copolymerized with perfluorinated monomer units. Many cure site monomers are known, including those with at least one bromo or iodo group. Such cure site monomers, when combined with a peroxide and a coagent, will provide a suitably cured composition.

One class of curable fluoroelastomers are cured using nitrile group-containing cure site monomers. These fluoroelastomers can be cured through a trimerization of the nitrile groups to form thermally stable triazine cross-links. The triazine cross-links are formed during a curing process using a catalyst. Generally, the most useful catalysts for such a cure are organotin compounds. Organotin compounds are, however, highly toxic and can

leave extractable metallic residues in the finished cured products into which they are incorporated. There is therefore a desire to eliminate or substantially reduce their use in commercial curing processes.

Summary of the Invention

As noted above, there is a need to eliminate or substantially reduce the use of organotin compounds in curable fluoroelastomer compositions and cured products made from them. The present invention does this by eliminating the need for organotin compounds in the catalyst system of the curable fluoroelastomer composition.

The fluoroelastomer compositions of the present invention employ at least one ammonia-generating compound as a catalyst to cure fluoroelastomers incorporating a nitrile group-containing cure site monomer. These compounds, when subjected to the conditions of curing, provide a source of ammonia that cures the fluoroelastomers without the need of a toxic, organotin catalyst.

In one aspect, the invention provides a curable fluoroelastomer composition comprising:

(1) a fluoroelastomer comprising interpolymerized units derived from (a) at least one perfluoroolefin; (b) at least one perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof; and (c) a cure site component comprising at least one nitrile group; and

(2) a catalyst composition comprising at least one ammonia-generating compound.

In another aspect, the invention provides molded articles, including O-rings, gaskets and seals, made from the above curable fluoroelastomer compositions.

In yet another aspect, the invention provides cured articles made from the curable compositions. These compositions are free from extractable metals such as tin. Also, the present invention provides a method for providing a curable fluoroelastomer composition free from extractable tin compounds and a method of stabilizing a curable fluoroelastomer composition against extraction of organometals such as tin.

The compositions of the invention retain the advantages of the use of nitrile group-containing cure site monomers. That is, they maintain the high temperature performance properties and chemical resistance typically achieved when organotin compounds are used in the catalyst system. At the same time, the compositions of the invention eliminate the

presence of extractable metal residues resulting from the use of organometal compounds, such as organotin, in the catalyst system.

The compositions of the invention, both the curable and cured compositions, are free of extractable organometal compounds. Consequently, they may be characterized as being pure. This result is achieved without the need to employ any additional processing steps to eliminate the organometal compounds. As a result, the compositions of the invention are useful in applications where polymer stability is important. The compositions of the invention are useful where thermal stability and chemical resistance are useful. They are also useful in silicon wafer fabrication because they eliminate the source of extractable metallic residues in the composition.

Detailed Description

Fluoroelastomers are polymeric compositions generally formed of interpolymerized units of at least two principal monomers. Generally, one of the monomers is a perfluoroolefin and the other is a perfluorovinyl ether, typically either a perfluoro(vinyl alkyl) ether or a perfluoro(vinyl alkoxy) ether. Representative of the perfluoroolefin monomers are tetrafluoroethylene and hexafluoropropene.

Suitable perfluorinated vinyl ethers include those of the formula:

$$CF_2{=}CFO(R'_fO)_a\,(R''_fO)_bR_f \qquad (1)$$

where:

R'_f and R''_f are the same or are different linear or branched perfluoroalkylene groups of 1-6 carbon atoms;

a and b are, independently, 0 or an integer from 1 to 10; and

R_f is a perfluoroalkyl group of 1-6 carbon atoms.

A preferred class of perfluoro(alkyl vinyl) ethers includes compositions of the formula:

$$CF_2{=}CFO(CF_2CFXO)_nR_f \qquad (2)$$

where: X is F or CF_3; n is 0-5, and R_f is a perfluoroalkyl group of 1-6 carbon atoms.

Most preferred perfluoro(alkyl vinyl) ethers are those where, in reference to either Formula 1 or 2 above, n is 0 or 1 and R_f contains 1-3 carbon atoms. Examples of such perfluorinated ethers include perfluoro(methyl vinyl) ether, perfluoro(ethyl vinyl) ether, and perfluoro(propyl vinyl) ether.

Other useful perfluorinated monomers include those compounds of the formula:

$$CF_2{=}CFO[(CF_2)_m(CFZ)_uO]_nR_f \qquad (3)$$

where R_f is a perfluoroalkyl group having 1-6 carbon atoms, m is 0-2, u is 0 or 1, n is 0-5, and Z is F or CF_3. Preferred members of this class are those in which R_f is C_3F_7, m is 0, and n is 1.

Additional perfluoro(alkyl vinyl) ether monomers useful in the invention include those of the formula:

$$CF_2{=}CFO[(CF_2CF(CF_3)O)_g(CF_2)_kO(CF_2)_p]C_xF_{2x+1} \qquad (4)$$

where g is 0 or an integer from 1-10, k is an integer of from 1-6, p is 0-3, and x is 1-5. Preferred members of this class include compounds where n is 0 or 1, m is 0 or 1, and x is 1.

Perfluoro(alkoxy vinyl) ethers useful in the invention include those of the formula:

$$CF_2{=}CFOCF_2CF(CF_3)O(CF_2O)_dC_eF_{2e+1} \qquad (5)$$

where e is 1-5, preferably 1, and d is 1-3. Specific, representative, examples of useful perfluoro(alkoxy vinyl) ethers include $CF_2{=}CFOCF_2OCF_2CF_2CF_3$, $CF_2{=}CFOCF_2OCF_3$, $CF_2{=}CFO(CF_2)_3OCF_3$, and $CF_2{=}CFOCF_2CF_2OCF_3$.

Mixtures of perfluoro(alkyl vinyl) ethers and perfluoro(alkoxy vinyl) ethers may also be employed.

Preferred fluorinated copolymers are composed of tetrafluoroethylene and at least one perfluoro(alkyl vinyl) ether as principal monomer units. In such copolymers, the copolymerized perfluorinated ether units constitute from about 15 to about 50 mole percent of total monomer units present in the polymer.

The fluorinated monomers of the invention may be polymerized by methods known in the art. For example, the polymerization process can be carried out by free-radical polymerization of the monomers alone or as solutions, emulsions, or dispersions in an organic solvent or water. Polymerization in an aqueous emulsion or suspension often is preferred because of the rapid and nearly complete conversion of monomers, easy removal of the heat of polymerization, and ready isolation of the polymer. Emulsion or suspension polymerization typically involves polymerizing monomers in an aqueous medium in the presence of an inorganic free-radical initiator system, such as ammonium persulfate or potassium permanganate, and surfactant or suspending agent.

Aqueous emulsion polymerization can be carried out continuously under steady-state conditions in which, for example, monomers, water, surfactants, buffers and catalysts are fed continuously to a stirred reactor under optimum pressure and temperature conditions while the resulting emulsion or suspension is removed continuously. An alternative technique is batch or semibatch polymerization by feeding the ingredients into a stirred reactor and allowing them to react at a set temperature for a specified length of time or by charging ingredients into the reactor and feeding the monomer into the reactor to maintain a constant pressure until a desired amount of polymer is formed.

The free-radical polymerization process can also be carried out in the presence of a perfluorosulfinate and an oxidizing agent to improve the processability of the resulting perfluoroelastomer composition. Such oxidizing agents are water soluble and capable of converting the sulfinate to a sulfonyl moiety. The produced sulfonyl radical is believed to eliminate SO_2 and form a fluorinated radical that initiates the polymerization of the ethylenically unsaturated monomers. A number of useful oxidizing agents are known as taught in U.S. Patent 5,285,002 and U.S. Patent 5,639,837. Representative examples of such useful oxidizing agents are sodium, potassium, and ammonium persulfates, perphosphates, perborates, percarbonates, bromates, chlorates and hypochlorites. Other useful oxidizing agents include cerium IV compounds such as $(NH_4)_2Ce(NO_3)_6$. The amount of oxidizing agent used can vary depending on the particular oxidizing agent and

sulfinate employed. Typically an equimolar amount or less (based on the amount of sulfinate) is used.

Perfluorosulfinates useful for this purpose include those described in U.S. Patent No. 5,285,002 and represented by the general formula:

$$R^3_fSO_2M_{1/x} \quad (6)$$

or

$$R^2_f[SO_2M_{1/x}]_j \quad (7)$$

where:

R^3_f represents a monovalent fluoroaliphatic radical having, for example, from 1 to 20 carbon atoms, preferably 4 to 10 carbon atoms;

R^2_f represents a polyvalent, preferably divalent, fluoroaliphatic radical having, for example, from 1 to 20 carbon atoms, preferably from 2 to 10 carbon atoms;

M represents a hydrogen atom or cation with valence x, which is 1 or 2; and

j is 1 to 4, preferably 1 or 2.

The amount of fluoroaliphatic sulfinate employed in the polymerization process can vary, depending, for example, on the molecular weight of polymer desired. Preferably the amount of fluoroaliphatic sulfinate is from 0.01 to 50 mole percent, and most preferably from 0.05 to 10 mole percent, of sulfinate compound based on total quantity of monomers.

In addition to the sulfinate, other reducing agents can be present, such as sodium, potassium or ammonium sulfites, bisulfite, metabisulfite, hyposulfite, thiosulfite, phosphite, sodium or potassium formaldehyde sulfoxylate or hypophosphite. Activators such as ferrous, cuprous, and silver salts, may also be present.

The cure site component employed in the invention is capable of curing the fluoroelastomer. The cure site component generally will comprise at least one nitrile group-containing cure site monomer. The cure site component can be partially or fully fluorinated. It will be understood that when the cure site component is fully fluorinated, the resulting polymer will be perfluorinated, and that when the cure site component is partially fluorinated, the resulting polymer will still be highly fluorinated. Useful nitrile

group-containing cure site monomers include nitrile-containing fluorinated olefins and nitrile-containing fluorinated vinyl ethers, such as depicted below:

$$CF_2{=}CFO(CF_2)_lCN \quad (8)$$

$$CF_2{=}CFO[CF_2CF(CF_3)O]_q(CF_2O)_sCF(CF_3)CN \quad (9)$$

$$CF_2{=}CF[OCF_2CF(CF_3)]_rO(CF_2)_tCN \quad (10)$$

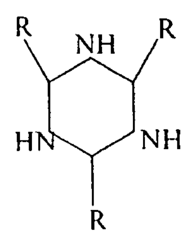
where, in reference to the above formulas: l=2-12; q=0-4; r=1-2; s=0-6; and t=1-4. Representative examples of such a monomer include perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene), $CF_2{=}CFO(CF_2)_5CN$, and $CF_2{=}CFO(CF_2)_3OCF(CF_3)CN$.

The curable fluoroelastomer compositions are cured using a catalyst comprising one or more ammonia-generating compounds. "Ammonia-generating compounds" include compounds that are solid or liquid at ambient conditions but that generate ammonia under conditions of cure. Such compounds include, for example, hexamethylene tetramine (urotropin), dicyan diamid, and metal-containing compounds of the formula:

$$A^{w+}(NH_3)_vY^{w-} \quad (11)$$

where A^{w+} is a metal cation such as Cu^{2+}, Co^{2+}, Co^{3+}, Cu^{+}, and Ni^{2+}; w is equal to the valance of the metal cation; Y^{w-} is a counterion, typically a halide, sulfate, nitrate, acetate or the like; and v is an integer from 1 to about 7.

Also useful as ammonia-generating compounds are substituted and unsubstituted triazine derivatives such as those of the formula:



wherein R is a hydrogen or a substituted or unsubstituted alkyl, aryl, or aralkyl group having from 1 to about 20 carbon atoms. Specific useful triazine derivatives include hexahydro-1,3,5-*s*-triazine and acetaldehyde ammonia trimer.

The fluoroelastomer compositions of the invention can be cured using one or more peroxide curatives along with the ammonia generating catalysts. Suitable peroxide curatives generally are those which generate free radicals at curing temperatures. Dialkyl peroxide and bis(dialkyl peroxide), each of which decomposes at a temperature above 50°C, are especially preferred. In many cases it is preferred to use a di-tertiarybutyl peroxide having a tertiary carbon atom attached to peroxy oxygen atom. Among the most useful peroxides of this type are 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexane. Other peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, tertiarybutyl perbenzoate, a,a'-*bis*(*t*-butylperoxy-diisopropylbenzene), and di[1,3-dimethyl-3-(*t*-butylperoxy)-butyl]carbonate. Generally, about 1 to 3 parts of peroxide per 100 parts of perfluoroelastomer is used.

The curable fluoroelastomer compositions can include any of the adjuvants commonly employed in curable fluoroelastomer formulations. For example, one material often blended with a fluoroelastomer composition as a part of the curative system is a coagent (sometimes also referred to as a co-curative) composed of a polyunsaturated compound that is capable of cooperating with the peroxide to provide a useful cure. These coagents can generally be added in an amount equal to between 0.1 and 10 parts per hundred parts fluoroelastomer, preferably between 1 and 5 parts per hundred parts fluoroelastomer. Examples of useful coagents include triallyl cyanurate; triallyl isocyanurate; tri(methylallyl isocyanurate; tris(diallylamine)-*s*-triazine; triallyl phosphite; N,N-diallyl acrylamide; hexaallyl phosphoramide; N,N,N',N'-tetraalkyl tetraphthalamide; N,N,N',N'- tetraallyl malonamide; trivinyl isocyanurate; 2,4,6-trivinyl methyltrisiloxane; and tri(5-norbornene-2-methylene)cyanurate. Particularly useful is triallyl isocyanurate.

Other useful coagents include the *bis*-olefins disclosed in EPA 0 661 304 A1, EPA 0 784 064 A1 and EPA 0 769 521 A1.

Additives, such as carbon black, stabilizers, plasticizers, lubricants, fillers, and processing aids typically utilized in fluoroelastomer compounding can be incorporated into the compositions of the invention, provided they have adequate stability for the intended service conditions. In particular, low temperature performance can be enhanced by incorporation of perfluoropolyethers. See, for example, U.S. Pat No. 5,268,405.

Carbon black fillers are typically also employed in elastomers as a means to balance modulus, tensile strength, elongation, hardness, abrasion resistance, conductivity, and processability of the compositions. Suitable examples include MT blacks (medium thermal black) designated N-991, N-990, N-908, and N-907, and large particle size furnace blacks. When used, 1-70 phr of large size particle black is generally sufficient.

Fluoropolymer fillers may also be present in the compositions of the invention. Generally, from 1 to 50 parts per hundred fluoroelastomer of a fluoropolymer filler is used. The fluoropolymer filler can be finely divided and easily dispersed as a solid at the highest temperature utilized in fabrication and curing of the fluoroelastomer composition. By solid, it is meant that the filler material, if partially crystalline, will have a crystalline melting temperature above the processing temperature(s) of the fluoroelastomer(s). Such finely divided, easily dispersed fluoroplastics are commonly called micropowders or fluoroadditives. Micropowders are ordinarily partially crystalline polymers. Examples of useful micropowders include low molecular weight PTFE, PFA, FEP and the like.

One or more acid acceptors can also be added to the formulations of the invention, though, where the presence of extractable metallic compounds is undesirable (such as for semiconductor applications) the use of inorganic acid acceptors should be minimized, and preferably avoided altogether. Commonly used acid acceptors include, for example, zinc oxide, calcium hydroxide, calcium carbonate, magnesium oxide, etc. These compounds generally are used in the fluoroelastomer formulation to bind any HF or other acids that might be generated at the high temperatures where fluoroelastomers must function.

The curable fluoroelastomer compositions of the invention may also be combined with other peroxide curable fluoroelastomer compositions. These other peroxide curable fluoroelastomer compositions typically employ small amounts of cure site monomers as a comonomer. Suitable cure site monomers are those which, when combined with a peroxide and, preferably a coagent, will provide a cured composition. Preferably these cure site monomers include at least one halo group (e.g., a bromo or an iodo group).

The curable compositions of the invention can be prepared by mixing the fluoroelastomer, the peroxide curative, the catalyst, the selected additive or additives, and the other adjuvants, if any, in conventional rubber processing equipment. The desired amounts of compounding ingredients and other conventional adjuvants or ingredients can be added to the unvulcanized fluorocarbon gum stock and intimately admixed or

compounded therewith by employing any of the usual rubber mixing devices such as internal mixers, (*e.g.*, Banbury mixers), roll mills, or any other convenient mixing device. For best results, the temperature of the mixture during the mixing process typically should not rise above about 120°C. During mixing, it is preferable to distribute the components and adjuvants uniformly throughout the gum for effective cure.

The mixture is then processed and shaped, for example, by extrusion (for example, in the shape of a hose or hose lining) or molding (for example, in the form of an O-ring seal). The shaped article can then be heated to cure the gum composition and form a cured elastomer article.

Pressing of the compounded mixture (*i.e.*, press cure) usually is conducted at a temperature between about 95°C and about 230°C, preferably between about 150°C and about 205°C, for a period of from 1 minute to 15 hours, typically from 5 minutes to 30 minutes. A pressure of between about 700 kPa and about 20,600 kPa is usually imposed on the compounded mixture in the mold. The molds first may be coated with a release agent and prebaked. The molded vulcanizate is then usually post-cured (e.g., oven-cured) at a temperature usually between about 150°C and about 300°C, typically at about 232°C, for a period of from about 2 hours to 50 hours or more depending on the cross-sectional thickness of the article. For thick sections, the temperature during the post cure is usually raised gradually from the lower limit of the range to the desired maximum temperature. The maximum temperature used is preferably about 300°C, and is held at this value for about 4 hours or more.

The curable compositions of the invention are useful in production of articles such as gaskets, tubing, and seals. Such articles are produced by molding a compounded formulation of the curable composition with various additives under pressure, curing the part, and then subjecting it to a post cure cycle. The curable compositions formulated without inorganic acid acceptors are particularly well suited for applications such as seals and gaskets for manufacturing semiconductor devices, and in seals for high temperature automotive uses.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of the present invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth hereinabove.

EXAMPLES

TEST METHODS

In the following examples, indicated results were obtained using the following test methods:

Press-Cure samples. Unless otherwise noted, 150 x 150 x 2.0 mm sheets were prepared for physical property determination by pressing at about 6.9 Mega Pascals (M Pa) for 10 minutes at 177°C.

Post-cure samples were prepared as described in the examples.

Tensile Strength at Break, Elongation at Break, and Modulus at 100% Elongation were determined using ASTM D 412-92 on samples cut from the press-cure or post-cure sheet with ASTM Die D. Units reported in Mega Pascals (M Pa).

Hardness was determined using ASTM D 2240-85 Method A with a Type A-2 Shore Durometer. Units are reported in points.

Compression set was determined on O-rings using ASTM 395-89 Method B. The O-rings had a cross-section thickness of 0.139 in. (3.5 mm.). After post-curing, the O-rings were compressed for 70 hrs at 200°C. Results are reported as a percentage of permanent set.

Example 1

A fluoroelastomer was prepared which contained 64.7 mole percent tetrafluoroethylene, 34.8 mole percent perfluoromethyl vinyl ether, and 0.5 mole percent of a nitrile group-containing cure site monomer, $CF_2=CFO(CF_2)_3OCF(CF3)CN$, by aqueous emulsion polymerization. The resulting polymer (100 g) was compounded with: 15 g of MT N990 carbon black, 5 g of zinc oxide, and 1 g of hexamethylene tetramine.

A sheet of the compounded admixture was pressed for 15 minutes at 177°C and subsequently post-cured under nitrogen using the following six stages of conditions: 25-200°C over 6 hours; 200°C for 16 hours; 200-250°C over 2 hours; 250°C for 8 hours; 250-300°C over 2 hours; and 300°C for 18 hours.

The cured samples were tested according to the indicated Test Methods, giving the following:

Tensile Strength at Break	11.8 MPa
Elongation at Break	290%
100% Modulus	3.6 MPa
Shore A Hardness	70
Compression Set	68.5%

After being subjected to heat aging for 10 days at 270°C, the samples were tested again, giving the following:

Tensile Strength at Break	7.1 MPa
Elongation at Break	337%
100% Modulus	2.7 MPa
Shore A Hardness	70

Examples 2-3

In Example 2, a fluoroelastomer of 63.8 mole percent tetrafluoroethylene, 34.8 mole percent perfluoromethyl vinylether, and 2.2 mole percent of a nitrile group-containing cure site monomer, $CF_2=CFO(CF_2)_5CN$, was prepared by aqueous emulsion polymerization. In Example 3, a fluoroelastomer of 61.9 mole percent tetrafluoroethylene, 36.4 mole percent perfluoromethyl vinyl ether, and 1.6 mole percent of a nitrile group-containing cure site monomer, $CF_2=CFO(CF_2)_3OCF(CF_3)CN$, was prepared by aqueous emulsion polymerization. In both cases, the resulting polymers (100 g) were compounded with: 20 g of MT N990 carbon black, and 1 g of hexamethylene tetramine.

Sheets of the compounded admixtures were prepared and tested as described in Example 1, giving the following properties:

	Example 2	Example 3
Tensile Strength at Break	16.0 MPa	12.8 MPa
Elongation at Break	98.2%	143%
100% Modulus	N/A	6.4 MPa
50 % Modulus	3.1 MPa	1.8 MPa
Shore A Hardness	71	66
Compression Set	13.5%	15.5%

Example 4

In Example 4, the fluoropolymer of Example 3 (100 g) was compounded with: 20 g of MT N990 carbon black and 1 g of acetaldehyde ammonia trimer trihydrate (available commercially from Fluka Chemie AG of Germany).

A sheet of the compounded admixture was pressed for 10 minutes at 177°C and subsequently post-cured for 16 hours at 230°C.

The cured samples were tested according to the indicated Test Methods, giving the following:

Tensile Strength at Break	10.5 MPa
Elongation at Break	303%
100% Modulus	3.2 MPa
Shore A Hardness	66

Example 5

In Example 5, a fluoroelastomer was prepared which contained 64.1 mole percent tetrafluoroethylene, 34.7 mole percent perfluoromethyl vinyl ether, and 1.2 mole percent of a nitrile group-containing cure site monomer, $CF_2=CFO(CF_2)_3OCF(CF_3)CN$, was prepared by aqueous emulsion polymerization. The resulting polymer (100 g) was compounded with: 25 g of MT N990 carbon black and 1 g of dicyan diamid.

A sheet of the compounded admixture was pressed for 45 minutes at 177°C and subsequently post-cured for 16 hours at 230°C.

The cured samples were tested according to the indicated Test Methods, giving the following:

Tensile Strength at Break	14.4 MPa
Elongation at Break	192%
100% Modulus	6.0 MPa
Shore A Hardness	72

Example 6

In this Example, 100 g of the fluoropolymer of Example 5 (64.1 mole % tetrafluoroethylene, 34.7 mole % perfluoromethylvinyl ether and 1.2 mole % cure site monomer of the formula $CF_2{=}CFO(CF_2)_3OCF(CF_3)CN$) was compounded with 15 g of N110 carbon black, 0.5 g of hexamethylene tetramine, 1.7 g of triallyl isocyanurate coagent (TAIC-DLC/72% active) and 0.8 g of peroxide (Varox™ DBPH-50/50% active).

A sheet of the compounded admixture was press cured for 30 minutes at 177° C and subsequently post cured under nitrogen as described in Example 1.

The cured sheets were tested according to the indicated Test Methods, giving the following results:

Tensile strength at break	14.2 MPa
Elongation at break	155%
100% Modulus	7.3 MPa
Shore A Hardness	80

CLAIMS

We claim:

1. A curable fluoroelastomer composition comprising:

(1) a fluoroelastomer comprising interpolymerized units derived from (a) at least one perfluoroolefin; (b) at least one perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof; and (c) a cure site component comprising at least one nitrile group; and

(2) a catalyst composition comprising at least one ammonia-generating compound.

2. The curable composition of claim 1 wherein said perfluoro(alkyl vinyl) ether is of the formula:

$$CF_2{=}CFO(R'_fO)_a\,(R''_fO)_bR_f \qquad (1)$$

where:

R'_f and R''_f are the same or are different linear or branched perfluoroalkylene groups of 2-6 carbon atoms;

a and b are, independently, 0 or an integer from 1 to 10; and

R_f is a perfluoroalkyl group of 1-6 carbon atoms.

3. The curable composition of claim 1 wherein said perfluoro(alkyl vinyl) ether is of the formula:

$$CF_2{=}CFO(CF_2CFXO)_nR_f \qquad (2)$$

$$CF_2{=}CFO[(CF_2)_m(CFZO)_u]_nR_f \qquad (3)$$

where n is 0-5; m is 0-2; u is 0 or 1; X is F or CF_3; Z is F or CF_3; and R_f is a perfluoroalkyl group of 1-6 carbon atoms;

$$CF_2{=}CFO[(CF_2CF(CF_3)O)_g(CF_2)_kO(CF_2)_p]C_xF_{2x+1} \qquad (4)$$

where g is 0 or an integer from 1-10, k is an integer of from 1-6, p is 0-3, and x is 1-5; or

$$CF_2{=}CFOCF_2CF(CF_3)O(CF_2O)_dC_eF_{2e+1} \qquad (5)$$

where e is 1-5 and d is 1-3.

4. The curable composition of claim 1 wherein said perfluorovinyl ether is selected from the group consisting of: perfluoro(methyl vinyl) ether, perfluoro(ethyl vinyl) ether, perfluoro(propyl vinyl) ether, $CF_2=CFOCF_2OCF_2CF_2OCF_3$, $CF_2=CFO(CF_2)_3OCF_3$, and $CF_2=CFOCF_2CF_2OCF_3$.

5. The curable composition according to claim 1 wherein said perfluoroolefin comprises tetrafluoroethylene.

6. The curable composition of claim 1 wherein said cure site component is a nitrile-containing monomer of the formula:

$$CF_2=CFO(CF_2)_lCN \quad (8)$$

$$CF_2=CFO[CF_2CF(CF_3)O]_q(CF_2O)_yCF(CF_3)CN \quad (9)$$

or

$$CF_2=CF[OCF_2CF(CF_3)]_rO(CF_2)_tCN \quad (10)$$

where l=2-12; q=0-4; y=0-6; r=1-2; and t=1-4.

7. The curable composition of claim 1 wherein said ammonia-generating compound is hexamethylene tetramine.

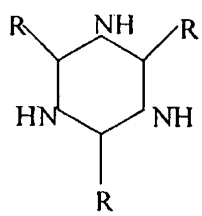
8. The curable composition of claim 1 wherein said ammonia-generating compound is dicyan diamid.

9. The curable composition of claim 1 wherein said ammonia-generating compound is a metal-containing compound of the formula:

$$A^{w+}(NH_3)_vY^{w-} \quad (11)$$

where A^{w+} is a metal cation; w is equal to the valance of the metal cation; Y^{w-} is a counterion; and v is an integer from 1 to about 7.

10. The curable composition of claim 1 wherein said ammonia-generating compound is of the formula:



wherein each R is hydrogen, or a substituted or unsubstituted alkyl, aryl, or aralkyl group having from 1 to about 20 carbon atoms.

11. A method of curing a fluoroelastomer composition comprising curing a fluoroelastomer comprising interpolymerized units derived from (a) at least one perfluoroolefin; (b) at least one perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof; and (c) a cure site component comprising at least one nitrile group in the presence of a catalyst composition comprising at least one ammonia-generating compound.

12. The method of claim 11 wherein said catalyst composition is substantially free of organotin compounds.

13. The method of claim 11 wherein said ammonia-generating compound is hexamethylene tetramine.

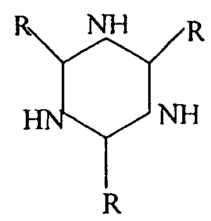
14. The method of claim 11 wherein said ammonia-generating compound is dicyan diamid.

15. The method of claim 11 wherein said ammonia-generating compound is a metal-containing compound of the formula:

$$A^{w+}(NH_3)_vY^{w-} \qquad (11)$$

where A^{w+} is a metal cation; w is equal to the valance of the metal cation; Y^{w-} is a counterion; and v is an integer from 1 to about 7.

16. The method of claim 11 wherein said ammonia-generating compound is of the formula:



wherein each R is hydrogen, or a substituted or unsubstituted alkyl, aryl, or aralkyl group having from 1 to about 20 carbon atoms.

17. An article made by the method of claim 11.

18. An O-ring made according to the method of claim 11.

19. The curable composition of claim 1 further including one or more peroxide curatives.

20. The curable composition of claim 1 essentially free of extractable organometal.

21. A method of providing a curable fluoroelastomer composition free from extractable organometal compounds comprising the steps of:

a) providing a fluoroelastomer having interpolymerized units derived from (i) at least one perolefin, (ii) at least one perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof, and (iii) a cure site component comprising at least one nitrile group, and

b) combining the fluoroelastomer with a catalyst system free from organometal compounds.

22. The curable composition of claim 1 further comprising (i) a peroxide curable fluoroelastomer composition having a cure site derived from a peroxide curable monomer, (ii) a peroxide curative, and (iii) optionally a coagent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03205

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K3/28 C08K5/16 C08K5/3492 C08L27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 09603 A (DUPONT DOW ELASTOMERS LLC) 24 February 2000 (2000-02-24) claims; examples	1-22
X	EP 0 735 095 A (NIPPON MEKTRON KK) 2 October 1996 (1996-10-02) claims; examples	1-6,11, 12,17, 18,20,21
X	US 5 677 389 A (LOGOTHETIS ANESTIS LEONIDAS ET AL) 14 October 1997 (1997-10-14) claims; example 5	1-6,11, 12,17, 18,20,21

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 June 2000	28/06/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	DE LOS ARCOS, E

2

Form PCT/ISA/210 (second sheet) (July 1992)

Inte nal Application No
PCT/US 00/03205

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 197914 Derwent Publications Ltd., London, GB; Class A14, AN 1979-27308B XP002140056 & SU 606 867 A (GALIL OGLY F A), 3 May 1978 (1978-05-03) abstract -----	1-6,11, 12,17, 20,21

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/03205

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0009603	A	24-02-2000	NONE		
EP 0735095	A	02-10-1996	JP	9111081 A	28-04-1997
			DE	69602665 D	08-07-1999
			DE	69602665 T	21-10-1999
			US	5565512 A	15-10-1996
US 5677389	A	14-10-1997	EP	0939785 A	08-09-1999
			WO	9823675 A	04-06-1998
SU 606867	A	15-05-1978	NONE		